CHAPTER I

C(Aryl)-H Bond Activation by Cyclometallation : An Overview and Purpose of the Present Investigation

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Abstract

A brief survey on the area of C(aryl)-H bond activation following cyclometallation route has been made with an emphasis on recent advances. In this background, the scope and purpose of the present investigation have been delineated.

I.1 Introduction

The activation of C-H bonds in organic compounds promoted by transition metal complexes has experienced a rapid growth in view of its diverse synthetic potential [1-7]. The central problem of C-H activation is to develop ways to replace target H substituents of organic molecules by any function groups, X (equation 1).

$$C–H \rightarrow C–X \qquad (1)$$

In spite of substantial work on the problem there is still no general method for the selective and efficient functionalization of inert C–H bonds. Apart from the academic interest, the field of C–H bond activation is of significant practical interest in relation to energy production. In this regard, the conversion of methane into methanol or conversion of *n*-alkanes to linear alcohols or carboxylic acids is worth mentioning.

However, one of the principal challenges in the field of C-H bond activation that limits its synthetic relevance is rooted in selectivity. Transition metal complexes that cleave C-H bonds are necessarily high in energy and therefore, controlling the chemo-, regio- and stereoselectivity of the C-H cleavage in a complex organic molecule, where C-H bonds are ubiquitous, is extremely difficult.

Biological systems often tackle these issues of C-H activation in elegant ways. A number of enzymes can oxidize unactivated C-H bonds, usually *via* hydroxylation [8-10]. Alkane activation is also reminiscent of dinitrogen fixation [11] to give ammonia and water oxidation [12] to oxygen in a sense that all these three processes involve inert substrates. In each case, a metalloenzyme carries out the key reaction. Therefore, significant efforts have been devoted to mimic the structural aspects of these enzymes to develop selective and efficient methods for C-H bond activation [13-15]. However, despite notable advances in this regard, the chemists are still far from the goal.

An alternative strategy to activate unreactive C-H bonds is based on cyclometallation reaction [16-27]. Despite being the mildest route, this particular route has received much less attention. In cyclometallation, the metal centers, precoordinated to a Lewis basic heteroatom group of the organic substrate, are brought in the vicinity of the C-H bond to be activated, which ultimately leads to the formation of a metal-carbon bond. This step is generally followed by functionalization at the metallated carbon resulting in the formation of functionalized hydrocarbons.

This chapter will focus primarily on the activation of C-H bonds by transition metal complexes in general, and C(aryl)-H bond in particular.

Our discussion in this chapter will be restricted to the various aspects of C(aryl)-H bond activation, with emphasis on the work done on the titled area and future directions that the field can offer.

2 Transition metal mediated C-H bond activation

2.1. Early studies

The Dimroth reaction, discovered as early as 1898 is often regarded as the first example of C–H bond activation. However, many scientists argued that Dimroth reaction could not qualify as C–H bond activation reaction as it was an eletrophilic attack on an π-arene system followed by the deprotonation of the resulting cation[28]

Another early achievement of C – H bond activation was reported by Fenton [29] in which hydrogen peroxide and iron(III) salts were used to hydroxyate alkanes, but with poor conversion yields. Fenton chemistry, also called Haber-Weiss chemistry, is believed to release HO˙ radicals [30-32] by Fe-catalyzed decomposition of H_2O_2 *via* steps as shown below

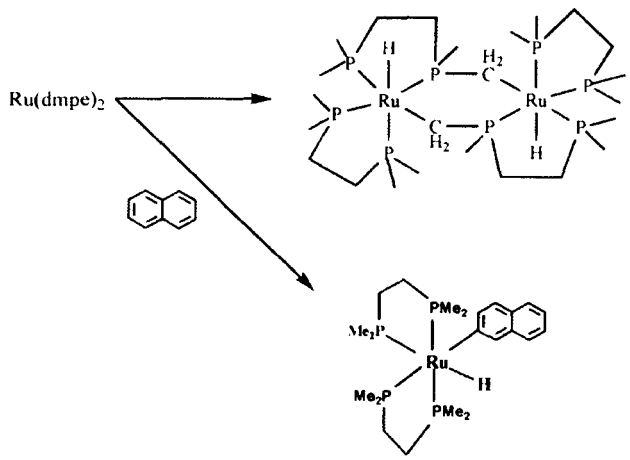
$$Fe(II) + H\text{-}O\text{-}O\text{-}H \rightarrow Fe(III) + OH^- + {}^{\cdot}OH$$

$$R\text{-}H + {}^{\cdot}OH \rightarrow R^{\cdot} + H\text{-}O\text{-}H$$

$$R^{\cdot} + O_2 \rightarrow R\text{-}O\text{-}O^{\cdot}$$

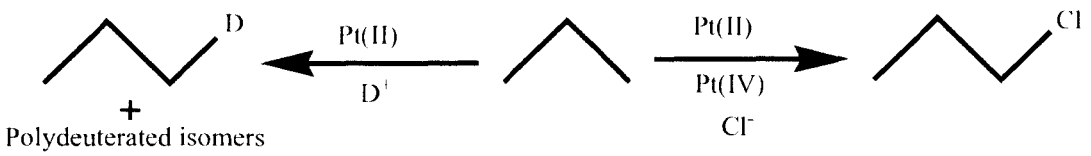
These radicals then react with alkane to form carbon radicals. The HO-H bond dissociation energy (BDE) of 119 kcal mol^{-1} easily allows HO˙ to abstract an H atom from an sp^3 C-H bond (typical BDE range 90-105 kcal mol^{-1}). The ROO˙ radical then goes on to give the observed products, such as alcohol and ketone.

In 1965, the first example of C–H bond activation by a transition metal complex resulting in the formation of a ruthenium phosphinomethyl complex with oxidative addition driven by chelate effect (II) and an intramolecular ruthenium phosphino naphthalene complex (III) was reported by Chatt [33]. This is regarded as the first example of cyclometalation involving sp^2 C–H bond (Scheme 1.1).



Scheme I.1

A new phase in C-H bond activation was given a thrust in 1972 by Shilov [34]. The Shilov chemistry invoves the addition of Pt(IV) to the aqueous reaction of $PtCl_4^{2-}$ with methane leading to the production of the selectively oxidized species methanol and methyl chloride. Despite the impractical use of platinum as a stoichiometric oxidant, this thirty year old "Shilov System" [35, 36] remains to date one of relatively few catalytic systems that actually accomplishes selective alkane functionalization under mild conditions (Scheme I.2). The system was revisited by Labinger and Bercaw [37, 38] and they reaffirmed the mechanistic routes offered by Shilov.

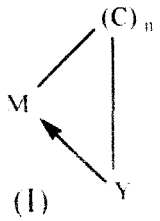


Scheme I.2

At the end of 1980s, interest gradually shifted to the oxidation of hydrocarbons by high valent metal-oxo compounds and dioxygen [39,40]. Different chemically significant hydrocarbon oxidation systems based on metal complexes of porphyrins [41,42], salens [43,44], corroles[45,46] have been developed. The non-heme catalytic systems [47,48] have also provided an active area of interest in expanding the scope and potential use of catalysts in bringing about C–H bond activation.

2.2. Cyclometallation reactions: an alternative route for selective C–H bond activation

Cyclometallates are the organometallic intramolecular coordination compounds with a ring system in which the metal has an intramolecular coordinate bond with a donor atom as well as a covalent metal-carbon bond (Scheme 1.3). Cyclometallation reactions afford interesting intermediates (**I**), which are known as cyclometallates; the term being introduced by Trofimenko [49].

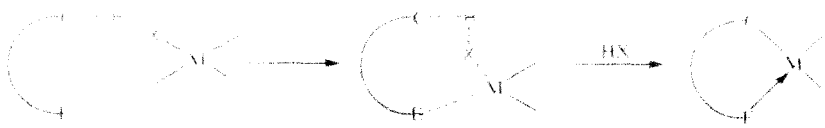


(I)

M= metal ion, Y = Coordinating atom, n = preferably 3 or 4

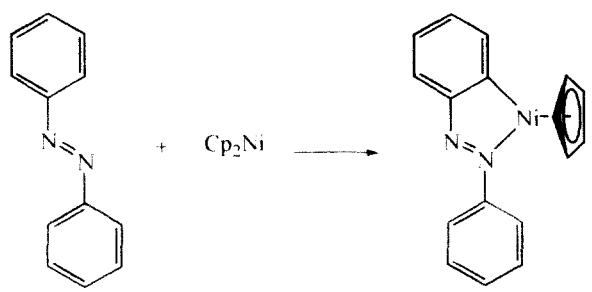
Scheme 1.3

In cyclometallation reactions, C–H bond activation is preceded by binding of substrate with a metal complex with or without minor rearrangements (Scheme 1.4). It is followed by stabilization of metal substrate complex or may lead to the targeted functionalization of the substrate and regeneration of the metal complex.



Scheme 1.4 C–H bond activation *via* cyclometallation

Cyclometallation was first reported in 1955 as synthetic reactions involving main group metal compounds [50]. On the other hand, the reaction of azobenzene with nickelocene (Scheme 1.5) reported in 1963 is generally regarded as the first reaction of cyclometallation by a transition metal [51].



Scheme 1.5

Professor Omae [16] classified the cyclometallated complexes as per the type of metal–carbon bond formed. Cyclometallates containing M–C σ-bonds are further classified on the basis of hetero donor atoms. On the other hand, cyclometallates containing M–C π-bonds has been classified on the basis of the nature of donating groups. A schematic representation of the classification has been provided in Table I.1.

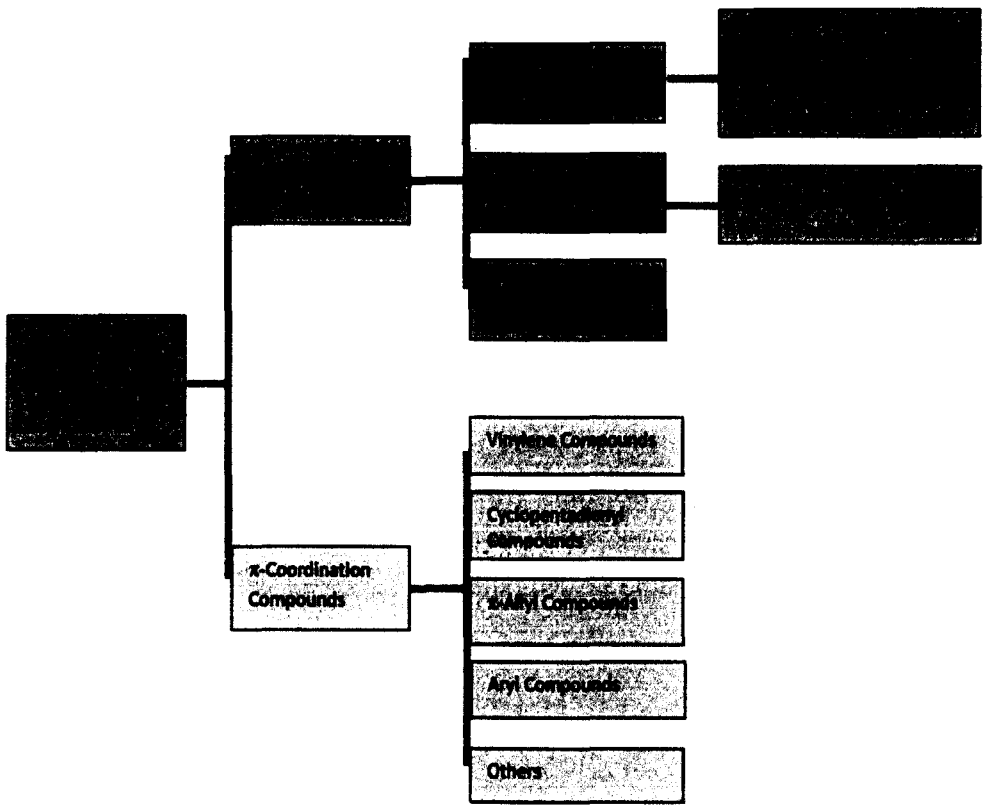
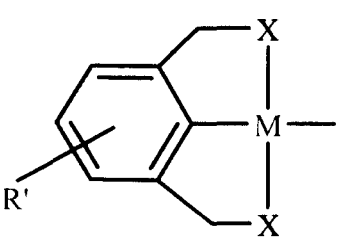


Table I.1 Classification of cyclometallates (adapted from Ref.16)

Furthermore, Professor van Koten developed a new group of cyclometallates based on the mode of coordination of ligands, termed as *pincer* complexes **(6)** [52-54].



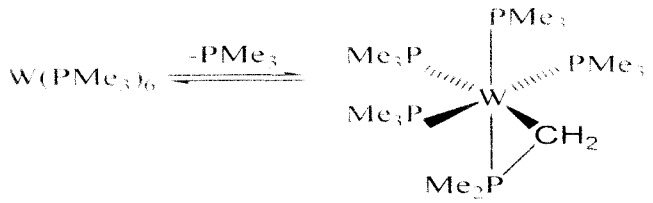
(II)

X= $-NR_2$, $-PR_2$, -SR

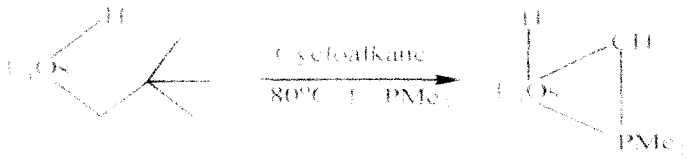
M=Metal ion

There has been a considerable interest in the chemistry of cyclometallated compounds [16-27]. Besides providing unusual coordination environments [55], the

cyclometallates find their applications in organic transformation, photophysics, metallomesogens and catalysis[56-66]. Some important examples of the cyclometallation of sp^3- and sp^2-C-H bonds have been presented in Scheme I.6.



Ref. 67



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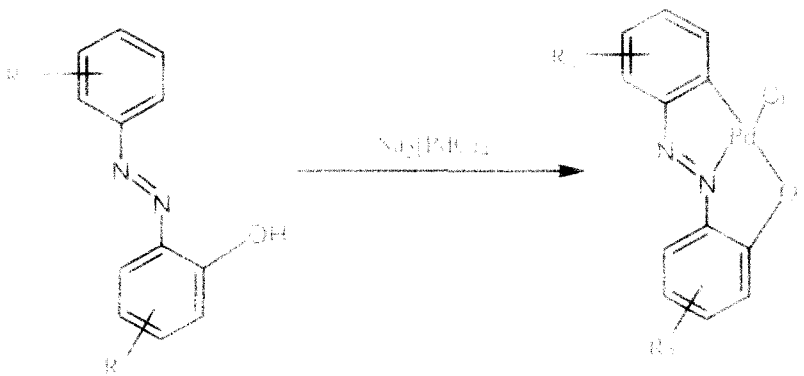

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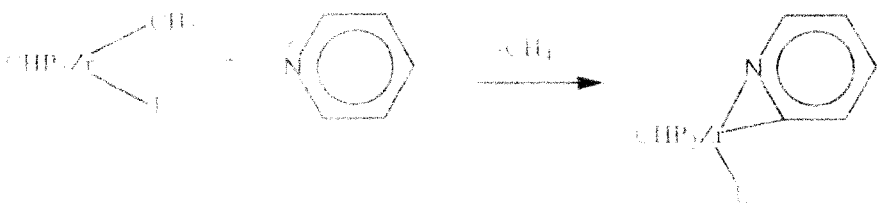

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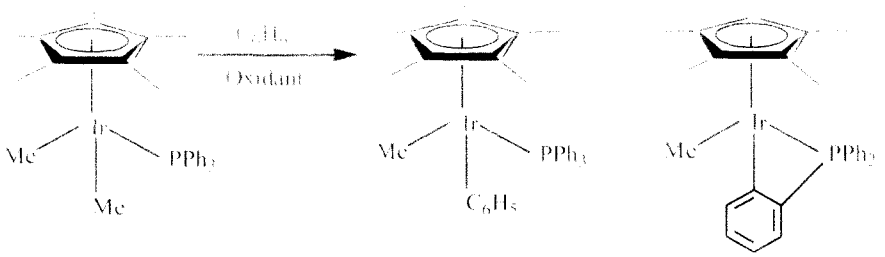

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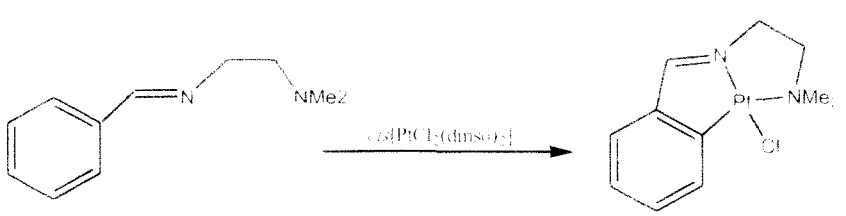

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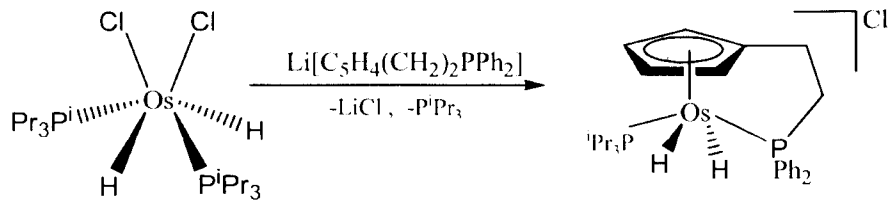

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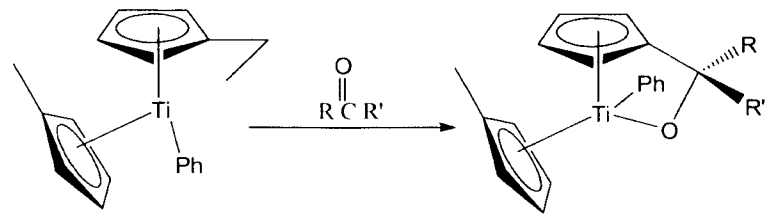

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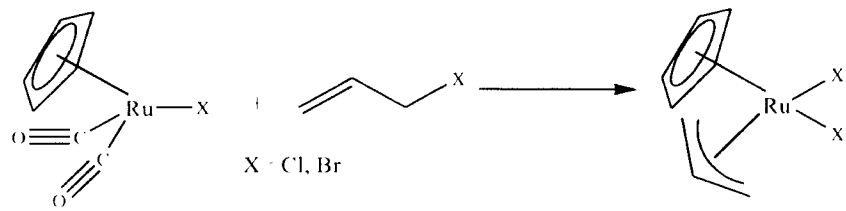

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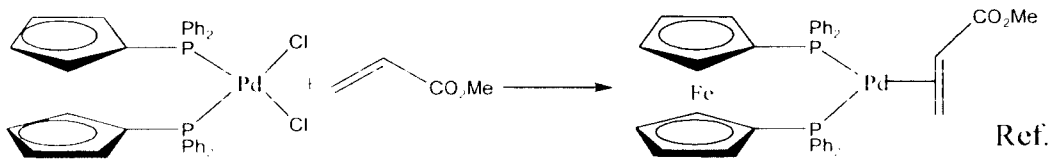

Ref.76

Scheme I.6 Selected examples of the cyclometallation of sp^3- and sp^2-C–H bonds

2.3. Role of additional or auxiliary donor in Cyclometallation reactions for selective C(aryl)-H bond activation

Selective activation of a particular C–H bond within a complex organic molecule is a challenging task. In such cases, the metallation is usually directed to a particular C–H bond by introducing a coordinating group (usually termed as the primary donor) at a suitable position within the substrate, which ultimately leads to the formation of metal-carbon bond [77-79]. In general, the C(phenyl)–H bond adjacent to the primary donor is activated and the process is called *orthometallation*. For example, in azobenzene, the C(phenyl)–H bond adjacent to the primary diazene group is activated following cyclometallation route (Scheme I.5).

On the other hand, several organic molecules having primary donor at a given position may possess more than one non-equivalent C–H bonds as potential metallation sites. For example, the cyclometallation of naphthyl group or fused ring

systems having N-donor pose interesting question regarding the selectivity of the C–H bond activation, due to the presence of more than one non-equivalent C–H activation sites. Rys *et al.* showed that that the metallation of 1-naphthylazoarenes with palladium(II) takes place at the *ortho*-position (C2) of the naphthyl ring, whereas the *peri*-palladation can only be achieved by blocking all the *ortho*-positions of the naphthyl rings [80]. Later on, our research group showed that the incorporation of suitable auxiliary donor at a position away from the target C–H bond can significantly influence the selectivity of C–H activation [81, 82] (Scheme I.7).

Scheme I.7

The Mechanistic Pathway of Cyclometalation

There are several reviews which primarily summarize the mechanistic details of C–H bond activation *via* cyclometalation route [16-27, 83]. The three major cyclometalation pathways [27] are as follow:

(i) Electrophilic bond activation

(ii) Oxidative addition

(iii) σ- Bond metathesis

However, it should be noted here that the exact process mechanism is still uncertain and many of the experimental observation have brought forth a diverse range of cyclometalated complexes. This often depends on the nature of the metal under investigation and the variation of the donor sites.

(i) Electrophilic bond activation

C–H bond activation by the electrophilic bond activation process is generally observed for late transition metals. An exemplary case is the C(aryl)–H bond activation by Pd(II) or Pt(II). It has been observed that the activation of C(aryl)–H bond gets facilitated with the introduction of an electron donating substituent in the aromatic ring, which closely resembles the general aromatic electrophilic substitution

reactions. The difference arises from the fact that the generation of a crucial π-complex prior to the formation of a σ-complex is not observed unlike electrophilic aromatic substitution [84], Reports of C-H bond activation in NCN pincer scaffolds give light to the above mentioned analogy [85]. The electrophilic cyclometalation pathway can be schematically represented as Figure I.3.

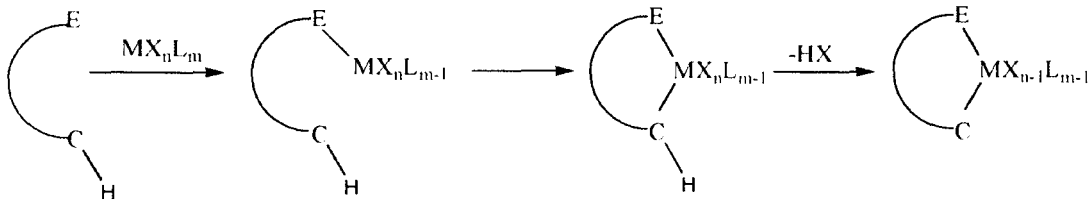

Figure I.3.

(ii) Oxidative addition

C–H or C–R bond activation requires electron rich metal centres. Ir(I) and Rh(I) are extensively used as metal precursors [86-88] in this type of reactions. Oxidative addition can be primarily distinguished from electrophilic cyclometalation on the basis of different roles played by C–H bonds of the substrates. In the electrophilic process the electron-donating interactions of the substrate predominate, whereas the substrate in oxidative addition is primarily an acceptor. Conceptually, the process can be summarized as given in Figure I. 4.

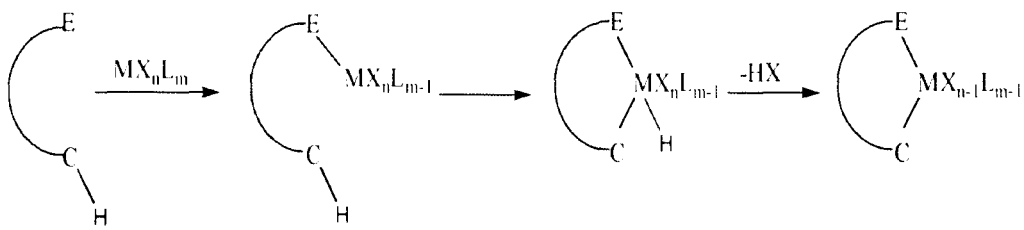

Figure I.4

(iii) σ- Bond metathesis :

When electron poor metal centers such as high valent early transition elements are involved in the cyclometalation process and perhaps also with carbonyl complexes, the σ-bond metathesis pathway is the plausible pathway. The general process has been depicted in Figure I.5.

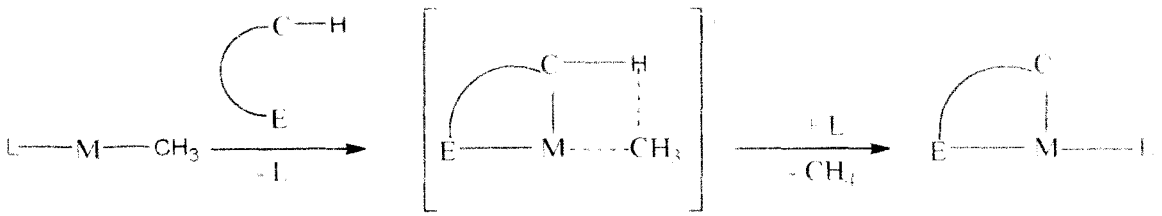

Figure I.5

Such metathesis have been reported also for late transition metals, however they have been presented in a modified form [89-90].

I.5. Purpose of the present work

The present status of the cyclometallation reactions led us to focus our work on the followings.

(i). The regioselective or regiospecific C(aryl)–H bond activation by transition metals utilizing cyclometallation route followed by isolation and characterization of the resulting cyclometallates.

(ii). The insertion of oxygen into C(aryl)–M bond of cyclometallates with an aim to functionalize metallated aryl carbon i.e. C(aryl)–M ⟶ C(aryl)–O–M.

Details of the purpose and work plan are described below.

Cyclometallation reaction (C–H ⟶ C–M) provides valuable insight into C–H bond activation process. The presence of hetero donor atom or functional group in the organic substrate activates the metal ion which in turn triggers the suitably oriented C–H bond of the target molecule resulting in M–C bond formation. The available literature mainly shows that the study of C–H bond activation of aromatic rings by cyclometallation have remained confined mainly within the area of C(phenyl)–H bond activation. Reports of C–H bond activation of other aromatic rings are relatively sparse[91-103].

Selective C(aryl)–H bond activation following cyclometallation route is an important field of research which requires detailed investigation. We wish to address the following issues:

(a) Selective activation of C(aromatic)–H bonds where more than one possible site for C–H activation is available.

(b) Role of the additional or auxiliary donor group on selectivity of C(aryl)–H activation.

(c) The roles of different metal ions in the selective C(aryl)–H bond activation.

In order to address the above mentioned issues, we wish to adopt the following strategy:

1. Our aim is to study the comparative ease of activation for different types of C(aryl)–H bonds, where more than one C(aryl)–H bonds are accessible by metal ions. Therefore, *regioselectivity* or *regiospecificity* of the processes is a core issue. Here, non-equivalent C–H bonds of naphthyl group have been chosen as target fragment.

2. The diazene group is well known to bind different metal ions in their different oxidation states. For this reason the diazene group has been chosen as primary donor, which is to be attached with the target naphthyl group to promote the site-selective activation of C(naphthyl)–H bonds.

3. Furthermore, a strategy has been drawn to incorporate an additional or auxiliary donor group in the organic substrates in such a manner that auxiliary donor group, capable of binding the metal ion, would remain away from the target naphthyl group. The influence of the auxiliary donor on the selection of metallation site would be investigated. Here, sulfinyl group is to be used as auxiliary donor, which offers either O or S donor towards metal ions.

4. The choice of metal ions is to be restricted to *'soft'* metal ions like palladium (II), platinum(II), ruthenium(II), rhodium(I) and iridium(I) ions for the activation of C(naphthyl)–H bond. The reactivity with *'less soft'* metal ions like ruthenium(III) , rhodium(III) and iridium(III) would also be examined.

5. To explore the scope of C–S bond cleavage (desulfurization), the role of valence state, stereochemistry and donor environment around the metal precursors would be investigated.

6. Attempts would be made to isolate the end products containing M–C(naphthyl) bond, formed in the process of C(naphthyl)–H bond activation by different metal ions. The characterization of new cylometallates would be done using different spectroscopic techniques and X-ray diffraction method.

7. The electronic structures of representative cyclometallates would be studied using Time Dependent Density Functional Theory (TD-DFT) in order to gain insights into the transitions of their electronic spectra.

8. The oxidative addition of electrophiles to cyclometallates would be examined.

9. The oxygen insertion into C(aryl)–M bond leading to the functionalization at metallated carbon i.e. C(aryl)–O–M (*metaloxylation*) would be investigated in details. The metaloxylation reactions would be studied following both stoichiometric and catalytic routes.

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